



Bio-based and environmental input for transfer hydrogenation using EcoNi(0) catalyst in isopropanol



V. Escande ^a, C. Poullain ^a, G. Clavé ^a, E. Petit ^b, N. Masquelez ^b, P. Hesemann ^c, C. Grison ^{a,*}

^a Laboratoire de Chimie Bio-inspirée et d'Innovations Ecologiques, ChimEco, UMR 5021 CNRS – UM, Cap Delta, 1682 Rue de la Valsière, 34790 Grabels, France

^b Institut Européen des Membranes, UMR 5635, CC 047, Place Eugène Bataillon, 34095 Montpellier, France

^c Institut Charles Gerhardt de Montpellier, UMR 5253 CNRS-UM-ENSCM, Université de Montpellier, Place E. Bataillon, Bât 17, CC 1701, 34095 Montpellier, France

ARTICLE INFO

Article history:

Received 26 January 2017

Received in revised form 2 April 2017

Accepted 6 April 2017

Available online 11 April 2017

Keywords:

Sustainable chemistry

Ecocatalysis

Bio-sourced catalyst

Reduction

Phytoextraction

ABSTRACT

The transfer hydrogenation of carbonyl compounds into alcohols with isopropanol has emerged as a green alternative to the use of hazardous reducing agents. Ni(0) nanoparticles have been described as an efficient catalyst for this reaction, while their classical preparation is still associated with a number of safety and environmental concerns. Here, we report a sustainable, ecological and straightforward preparation of a biosourced Ni(0) based material, by thermal decomposition of Ni(II) formate made from a Ni hyperaccumulating plant. The resulting catalyst, EcoNi(0), shows high catalytic activity and selectivity for the transfer hydrogenation of carbonyl compounds, including challenging aldehydes. The process seeks to be an incentive for the economic development of phytoextraction.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Mining and metallurgical operations are in the top for the metal waste production. They are problematic, because they are not biodegradable and persistent in organisms and ecosystems. These environmental issues can be addressed by an ecological solution, called phytoextraction [1–3]. Phytoextraction has emerged as a novel approach to clean up metal-polluted soils in which plants are used to transfer metal trace elements (TE) from soils to shoots. This phytotechnology leads to the development of a vegetative cover, which forms a protection against wind and water erosion of TE. It is among the less costly technologies of soils remediation and has a good public acceptance [4]. However, TE concentration in plant leaves is high enough to generate new contaminated wastes.

Our group has shown that these plant wastes produced could be recovered using an innovative concept of sustainable chemistry. Taking advantage of the remarkable adaptive capacity of some plants to hyperaccumulate metals, ecocatalysis is based on the original use of metal species of plant origin as catalysts in fine organic chemical reactions. This allows the preparation of

biomolecules using an eco-responsible and bio-inspired approach [5]. The obtained results demonstrate that these new polymetallic catalysts present a unique chemical structure [6–8]. They offer new opportunities for cooperative catalysis within the synergy between metals [9–11], and present huge potential for the future [12]. Their activities, chemoselectivity and recyclability are higher than traditional catalysts in many reactions [13–15]. Ecocatalysts constitute an entirely new generation of efficient green oxidative catalysts [16], Lewis acid catalysts [17], and sustainable C–C formation agents [18]. They can be used as alternative reagents to replace those prohibited by European REACH regulations [14,19].

Ecocatalysis brings a change in paradigm: biomass from phytoextraction is no longer considered as contaminated waste, but rather as a natural restoration system with high added value [20]. This biomass is a natural reservoir of transition metals, precious in organic synthesis. In other words, waste becomes a useful and innovative chemical tool.

However, the use of ecocatalysts as potential green reducing agents has never been studied. The interest of EcoNi in the area of reduction is thus promising for ecological and chemical reasons.

We have recently reported that biosourced polymetallic ecocatalysts EcoNi(II) prepared from biomass derived from Ni hyperaccumulating plants, could efficiently and selectively mediate different addition reactions on alkenes and aromatic compounds [20–22]. The synthetic protocols based on the use

* Corresponding author.

E-mail address: claude.grison@cnrs.fr (C. Grison).

of EcoNi(II) catalysts combined several advantages: low catalyst loading, high yields of reaction products, short reaction times, eco-friendly reaction conditions, high selectivity and the possibility of the catalyst recovery and reuse. Therefore, we envisaged the possibility of applying these EcoNi(II) materials as new bio-based feedstock to synthesize novel EcoNi(0) catalysts and to study their catalytic activity in the transfer hydrogenation of carbonyl compounds. In this communication, we show that greener reductions of ketones and aldehydes can be performed with high yield and selectivity, with a biosourced EcoNi(0) catalyst.

The reduction of the carbonyl group of aldehydes and ketones to the corresponding alcohols is among the most common transformations in organic synthesis. Since early reports of reduction by diborane, metal hydrides are some of the most important reagents for performing this synthetic transformation at the laboratory scale. Alkali and alkaline earth metal hydrides, boranes and derivatives, alanes and derivatives, metal borohydrides, metal aluminohydrides, silanes, stannanes and transition metal hydrides have been largely described [23]. The synthetic utility of these reagents is beyond question. However, in the context of Green Chemistry, the operating conditions and safety of the reagents/solvent/process are obvious drawbacks of this methodology. Workup procedures are hazardous to handle and generate a large amount of wastes as by-products. The reduction step is often carried out with a stoichiometric amount of metal hydride. The reduction of carbonyl compounds to alcohols by catalytic hydrogenation represents the main industrial alternative to the use of hazardous metal hydrides [24]. Currently, the preferred transition metals for hydrogenation of carbonyl compounds are Ru, Pt, Pd, Rh and Ni. However, these catalytic processes often require high temperatures and pressures, which can be an industrial risk. Another challenge associated with the catalytic hydrogenation of carbonyl group into alcohol is the cost of the metal catalyst. A major concern regarding the future availability of these metal elements is their resource depletion and the difficulty of access to metal deposits [25].

Transfer hydrogenation (hydrogen transfer, H-transfer) is an interesting alternative methodology for the reduction of carbonyl compounds. The first advantage of this process over catalytic hydrogenation is the elimination of safety restrictions associated with the use of high pressure and temperature. The first examples of H-transfer reduction of ketones were reported with aluminium alkoxides (Meerwein-Ponndorf-Verley (MPV) reduction). The main drawback of this method is the reversibility of the reaction, the necessity of using a stoichiometric amount of catalyst and the hazardousness of $\text{Al}(\text{O}i\text{Pr})_3$. A milestone was the discovery that metal complexes were able to catalyze the H-transfer reduction of ketones [26]. While a number of catalysts still rely on homogeneous complexes of expensive metals, such as Ru, Rh or Ir, several greener alternative catalysts have been proposed, including the use of heterogeneous catalysts. These materials comprise zeolites, hydrotalcite and various metal oxides, which are easily available and cheap [27,28]. However, their synthetic potential is often limited to small substrates and their use frequently requires high temperatures.

Dehydrated alumina supported KOH can also be used as an effective catalyst in the presence of isopropanol as a source of active hydride and solvent, under microwave irradiation [29].

A recent alternative is the description of H-transfer reduction of carbonyl compounds promoted by Ni(0) nanoparticles [30,31]. Good to high yields of the corresponding alcohols were obtained depending on the nature of the substrate. The Ni nanoparticles were reused several times, maintaining a high catalytic activity. In terms of Green Chemistry, this methodology raises however several issues: the mixture of THF/*i*-PrOH as solvent is less advantageous than the eco-friendly isopropanol solvent alone. The preparation of Ni(0) nanoparticles by reduction of Ni(II) with lithium powder and

a catalytic amount of DTBB (4,4'-di-*tert*-butylbiphenyl) in THF, was hazardous and exhibited a high environmental impact.

Improvements were thus required in order to meet the standards of current eco-friendly chemistry.

2. Experimental section

2.1. Reagents and methods

All reagents and solvents were purchased from Sigma-Aldrich and were used without further purification. Leaves of *Psychotria gabriellae* were harvested in New Caledonia, in the Mont Koghi locality. GC-MS analyses were performed using a Shimadzu QP2010SE, equipped with a $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$ ZB-5MSi Guardian column (Phenomenex[®]) with hydrogen as carrier gas. Inductively coupled plasma mass spectrometry (ICP-MS) analyses were performed using the metal analysis of total dissolved solutes in water. The samples were acidified with nitric acid 2.5% and stirred for 30 min. The digestes were diluted to 0.005 g L^{-1} . Three blanks were recorded for each step of the digestion and dilution procedure on a HR-ICP-MS Thermo Scientific Element XR. Three analyses were performed for each sample in order to determine the standard deviation of the measurement. X-ray diffraction (XRD) data measurements on the samples dried at $110\text{ }^\circ\text{C}$ for 2 h were performed by using a BRUKER diffractometer (D8 advance, with a CuK α radiation $\lambda=1.54086\text{ \AA}$) equipped with a LynxEye detector. TGA was performed with a TA Instruments Q500, under a flow of N_2 , on 14 mg of material. Nitrogen sorption experiments were performed using a Micromeritics Tristar apparatus. The specific surface area S_{BET} was calculated by the Brunauer-Emmett-Teller method (BET). Pore volume and average pore size were estimated using the Barrett-Joyner-Halenda method with the Kruk-Jaroniec-Sayari equation (BJH/KJS). All calculations were performed on the adsorption branch of the isotherm. Prior to analyses, the sample was outgassed overnight at $110\text{ }^\circ\text{C}$. XPS analyses were performed with an ESCALAB 250 spectrometer (Thermo Electron Corporation), using a monochromatized focused Al K X-ray source (1486.6 eV). The calibration of the spectrometer was done with Cu 2p3/2(932.8 eV), Au 4f7/2(84.0 eV) and Ag 3d5/2(368.6 eV). TEM images were taken using a Jeol 1200-EX2 Transmission Electron Microscope at accelerating voltage of 100 kV. EDS analysis with energy resolution 133 eV in scanning mode was performed using a Jeol JEM-2200FS Field Emission Electron Microscope at accelerating voltage of 200 kV. SEM images were obtained at the 'Institut Européen des Membranes', Montpellier, France, using a Hitachi S-4800 Field Emission Scanning Electron Microscope.

2.2. Preparation of EcoNi(II) formate

Leaves of *Psychotria gabriellae* were air-dried and crushed, then heated to $400\text{ }^\circ\text{C}$ under air for 5 h. The resulting powder (20 g) was heated in formic acid (400 mL) under stirring, to $90\text{ }^\circ\text{C}$ for 18 h. The resulting blue-green suspension was cooled to room temperature, then filtrated through a pad of Celite[®], rinsed with 100 mL of formic acid. The acid solution was discarded, then the resulting solid (mixture of insoluble formates and Celite[®]) was rinsed with $3 \times 100\text{ mL}$ of boiling water. The resulting bright green solution was collected by filtration, then concentrated under reduced pressure, affording EcoNi(II) formate as a light green solid (14.9 g).

2.3. Preparation of EcoNi(0)

The EcoNi(0) was obtained by thermolysis of EcoNi(II) formate. For this purpose, 180.7 mg of EcoNi(II) formate were placed in a tubular oven by the aid of a porcelain crucible. The sample was first

heated to 250 °C for 2 h in a nitrogen stream in order to eliminate volatile species. After this time, the nitrogen flux was stopped and the temperature was raised to 380 °C during 3 h. After cooling to room temperature, the EcoNi(0) was recovered as a black powder. Yield: 70.8 mg.

2.4. Representative procedure for ecoNi(0)-catalyzed H-transfer reduction

EcoNi(0) (1 mol%) and Al₂O₃ basic Brockmann I (1 g, activated by heating to 400 °C for 15 min) were added to a 25 mL flask containing *i*-PrOH (5 mL) and the carbonyl compound (1 mmol). The resulting mixture was magnetically stirred to 80 °C. The reaction progress was monitored by GC-MS analysis, with the following temperature programme: 4 min isothermal at 40 °C, then increasing from 40 °C to 270 °C at 20 °C·min⁻¹. GC-MS calibration was performed by analysis of known quantities of pure products and dodecane as an internal standard.

3. Results and discussion

We demonstrate here that EcoNi(0) prepared by thermal reduction of EcoNi(II) formate has high potential in green reduction of carbonyl compounds, and that this ecocatalyst is well adapted for the selective reduction of multifunctionalized compounds, including conjugated aldehydes.

3.1. EcoNi(0) preparation and characterization

3.1.1. TGA analysis and reduction of EcoNi(II) formate: formation of EcoNi(0)

We focused on the formation of a Ni(0) catalyst for H-transfer hydrogenation starting from biomass of a Ni-hyperaccumulating plant. Leaves were harvested from *Psychotria gabriellae* (Rubiaceae), a native Ni-hyperaccumulating plant of the subtropical Pacific island New Caledonia. They were collected from plants growing in the Southern Province of New Caledonia. By following a procedure described in previous reports [6,22], thermal treatment of this biomass under air afforded a powder consisting of oxides of the metal elements present in the plant. Among these oxides, nickel was present as NiO, so that a reduction to Ni(0) was required. Production of Ni(0) nanoparticles used as catalyst for H-transfer hydrogenation has been previously performed by reduction of Ni(II) salts with several reducing agents, such as metal lithium [31–35], hydrazine [36–40], NaBH₄ [41–43], ethylene glycol [44–46], oleylamine/triethylphosphine [47] or by thermal decomposition of nickel isopropoxide, prepared with an excess of Li, Na or K metal [48]. In spite of their efficiency, these reducing agents are toxic or hazardous to manipulate. The use of alkali metals in excess also raises sustainability issues, due to the high environmental footprint associated with their production. Formation of Ni(0) by reduction of bioaccumulated Ni(II) has been described in a previous report, by pyrolysis of wood of another Ni hyperaccumulating plant (tree *Sebertia acuminata* Pierre ex. Baillon), leading to Ni(0) supported on charcoal (Ni 5–7 wt%) [49]. However, the hyperaccumulating plant used was a rare, endangered species [50], and no catalytic activity of the material was reported. In order to produce Ni(0) in a sustainable way from bioaccumulated Ni(II), we selected the thermal reductive decomposition of Ni(II) formate.

Table 1
ICP-MS analysis of EcoNi(II) formate and EcoNi(0).

	wt% (±sd ^a)	
	EcoNi(II) formate	EcoNi(0)
Na	4.7 (±0.2)	17.0 (±1.3)
Mg	2.5 (±0.1)	4.1 (±0.3)
Ca	3.0 (±0.2)	10.2 (±0.5)
Ni	22.8 (±0.5)	40.7 (±2.9)
Mn	0.3 (±0.006)	0.7 (±0.05)
Fe	0.6 (±0.04)	0.9 (±0.06)

^a Standard deviation.

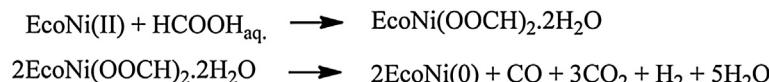
This procedure allows the formation of Ni(0) without the use of additional reducing agents. This particular behavior is related to the reducing character of formates/formic acid, which is able to reduce Ni(II) 'in situ' [51,52].

EcoNi(II) formate was firstly obtained by formic acid treatment of the mixture of oxides, resulting of the calcination of *P. gabriellae* leaves. As Ni(II) formate is not soluble in pure formic acid, EcoNi(II) formate was recovered by filtration as a solid containing 22.8 wt% Ni (Table 1). This value is slightly lower compared to the theoretically expected value, based on the chemical composition of nickel formate dihydrate (H₆C₄O₆Ni). The result is due to the presence of other metallic species of plant origin (Ca, Mg, Na, K, Fe). This intermediate nickel salt was used to access EcoNi(0) via a simple thermolytic step. In addition of avoiding costly and hazardous reducing agents, the use of formic acid is another sustainable asset, because this molecule can be produced from biomass feedstocks [53,54]. Here, we used this approach for the formation of biosourced Ni(0) catalysts, with high content in Ni, thanks to the elimination of carbon as CO and CO₂ (Scheme 1) [55–57].

For this reason, we then studied the thermal behavior of our EcoNi(II) formate via thermogravimetric analysis (TGA). The TGA plot of the material in the range of 50–1000 °C is given in Fig. S1. It clearly appears that the material shows three distinct weight loss steps. The first step, occurring at temperatures below 250 °C, is related to the elimination of physisorbed water and formic acid. The decomposition of the EcoNi(II) formate and the formation of EcoNi(0) occurs at temperatures 300 °C < T < 350 °C. This behavior is very similar to previously reported results obtained with pure Ni(II) formate, also showing a sharp mass loss at approx. 300 °C [52]. Finally, a last mass decrease can be observed at higher temperatures (T > 800 °C). This mass loss is due to further dehydration steps of metallic hydroxides and/or sublimation of various metallic species. In this context, it has to be pointed out that despite the fact that the material is mainly constituted of Ni species, a multitude of other metals (Na, Mg, Ca) is present (see Table 1).

In order to synthesize sufficient biosourced EcoNi(0) and to study its catalytic properties, we exploited this thermal reduction of Ni(II) formate into Ni(0) to access to on a larger scale (Fig. 1). We first heated EcoNi(II) formate to 250 °C for 2 h in a nitrogen stream in order to eliminate volatile species such as physisorbed water and formic acid. After this time, the N₂ stream was stopped in order to form a reducing atmosphere due to the decomposition of formate and the formation of carbon monoxide in the reactor. The material was further heated to 380 °C during 3 h in order to form the EcoNi(0).

This method can be advantageously compared to conventional processes, which required hazardous metallurgical preparation of



Scheme 1. Mechanism of formation of EcoNi(0) derived from nickel hyperaccumulating plant.

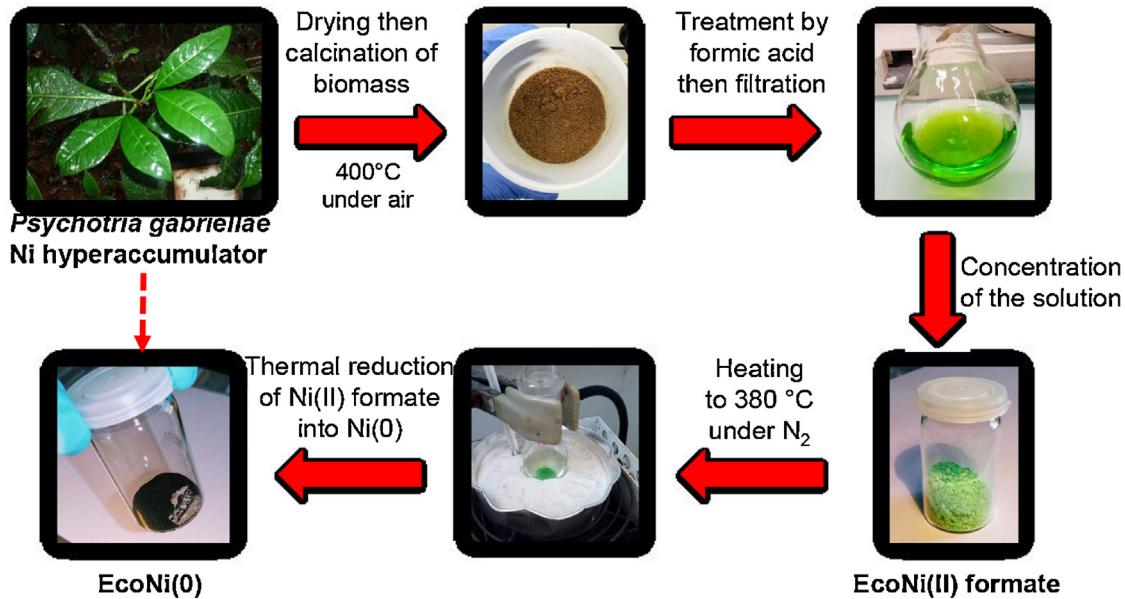


Fig. 1. Preparation of EcoNi(0) from Ni hyperaccumulator *Psychotria gabriellae*.

Ni precursors [58]. EcoNi(0) was characterized *via* ICP-MS, nitrogen sorption, scanning electron microscopy and X-ray diffraction in order to determine the chemical composition, surface properties and crystallinity of the material.

3.1.2. ICP MS analysis

As shown by ICP-MS study (Table 1), EcoNi(0) obtained as a black powder, is a polymetallic solid with Ni as the major transition metal (40.7 wt%). The reproducibility of composition of similar EcoNi(0) was studied, and showed that the levels of transition elements are only slightly variable between samples derived from different plants of the same species. In particular, results show the necessity of considering leaves age in the design of sample collection to obtain a constant TE content in batches of EcoNi(0) [59]. EcoNi(0) was prepared from several batches of *P. gabriellae* in order to homogenize the content and minimize possible variations in the composition. Updated data on Ni-hyperaccumulating and accumulating plants from New Caledonia have been presented in some recent papers of our group, aimed at producing EcoNi catalysts on industrial scale in view of their commercialization [60,61].

3.1.3. XRD characterization of EcoNi(0)

In order to confirm the chemical composition of EcoNi(0), we performed X-ray diffraction measurements with this material. Fig. 2 shows the X-ray powder diffractogram of EcoNi(0), obtained by thermolysis of EcoNi(II) formate. The diffractogram shows the characteristic diffractions rays of Ni(0), along with the unexpected alloy FeNi₃, whose formation can be explained by reduction of iron formate, present in small amount in EcoNi(II) formate (according to Fe wt% detected in ICP-MS, see above). Besides Ni(0) and FeNi₃, sharp diffraction rays at 14.7, 25.6, 29.7, 31.8 and 49.3° indicate the presence of calcium sulfate. Furthermore, the diffraction ray of low intensity at 62.9° suggests the presence of nickel oxide, probably formed during the sample preparation. Broadening of the corresponding peaks suggests the formation of small nickel particles, according to the Scherrer equation [62]. Subsequent characterization of EcoNi(0) morphology was thus conducted to determine the porosity and the particles size.

3.1.4. XPS analysis

X-ray photoelectron spectroscopy (XPS) with EcoNi(0) was performed in order to confirm the oxidation state of nickel in the EcoNi(0) material, after thermal decomposition of EcoNi(HCOO)₂.

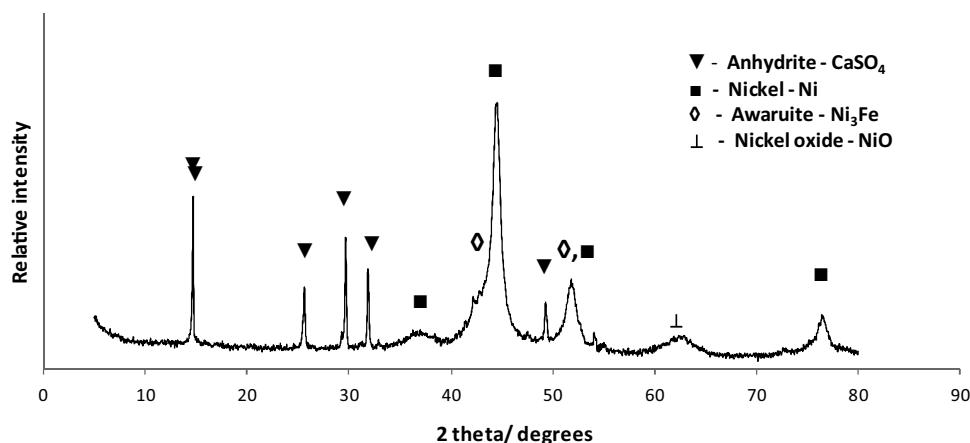


Fig. 2. X-ray diffractogram of EcoNi(0) and detected species.

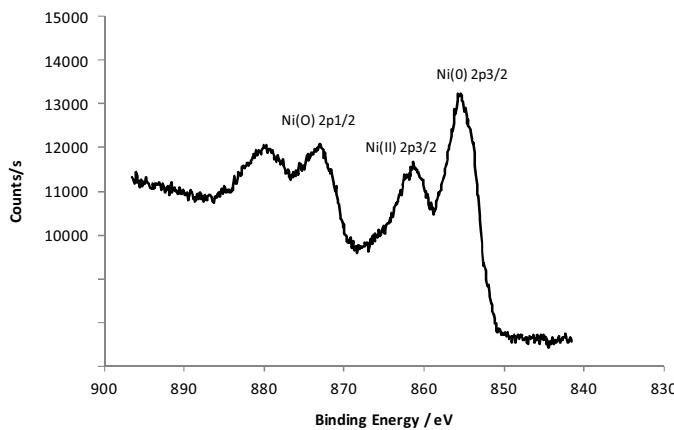


Fig. 3. XPS spectrum of EcoNi(0).

The Ni 2p core level XPS spectrum (Fig. 3) shows three peaks centered around 856, 861 and 873 eV, which can readily be assigned to Ni(0) 3p3/2, Ni(II) 2p3/2 and Ni(0)2p1/2, respectively. The peaks observed for Ni(II) 2p3/2 s could be assigned to the presence of NiO, that may originate from the surface oxidation of Ni(0) nanoparticles during the XPS sampling procedure. Ni(II) may be overestimated as XPS is a surface sensitive method which only takes into account the surface of the material. These observations are in agreement with the recently reported results of Zahmakiran et al. [63]

3.1.5. Characterization by nitrogen sorption and SEM

We studied the textural properties of the material *via* nitrogen sorption. The nitrogen sorption isotherm is given in Fig. 4. The isotherm shows that the EcoNi(0) is a moderately porous material with a specific surface area of $109 \text{ m}^2/\text{g}$ and a mesopore volume of $0.20 \text{ cm}^3/\text{g}$. The progressive nitrogen uptake over a quite large P/P_0 range indicates rather broad pore size distribution. Finally, the strong nitrogen uptake at high partial pressures indicates intergrain porosity and suggests that the material is constituted of agglomerated primary nanoparticles.

These results are confirmed *via* scanning electron microscopy (SEM). SEM images of the material clearly confirm the granular morphology of the material; with consists of agglomerated particles displaying a particle size in the range of 15–50 nm (Fig. 5b).

3.1.6. TEM analysis

The characterization of EcoNi(0) via Transmission Electron Microscopy (TEM) affords valuable information about the texture and homogeneity of the material. Two representative TEM images are given in Fig. 6. The material is constituted of particles of a diam-

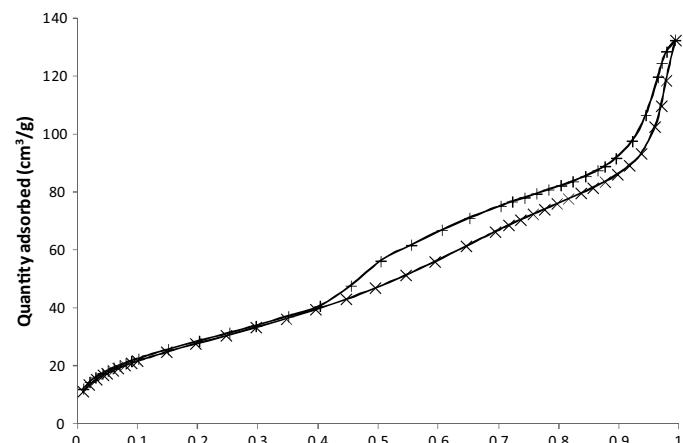


Fig. 4. Nitrogen sorption isotherm of EcoNi(0).

eter of several hundreds of nanometers. It clearly appears that these particles are heterogeneous and consist of at least two phases. Ni(0) nanoparticles of variable size can clearly be seen. The diameter of these particles is in the range of 2–20 nm. The Ni(0) particles are embedded within a matrix of a support material, probably calcium sulfate, as indicated by XRD and ICP-MS analysis.

3.1.7. EDS analysis

Finally, we performed Energy-dispersive X-ray spectroscopy (EDS) analysis in order to confirm the morphological features of the material and its chemical composition. EDS analysis with EcoNi(0) (see Supporting information) clearly shows that this material displays a heterogeneous morphology. Elemental mapping allows differentiating nickel rich domains with Ni contents up to 70 wt-% on the one side, and nickel poor domains with nickel content lower 10 wt-% and containing mainly calcium, sulfur and oxygen. This result therefore confirms the XRD analysis which indicated the presence of a significant amount of calcium sulfate in the material. EDS analysis also indicates the presence of small amounts of magnesium and manganese in the material, therefore confirming the results obtained by ICP-MS analysis.

In conclusion, TEM, SEM, XPS and EDS analysis give concordant results regarding the elemental composition and the morphology of the EcoNi(0) material. In fact, EcoNi(0) is constituted of Ni(0) nanoparticles which are embedded in a calcium sulfate matrix. Nickel poor and nickel rich domains are present in the same particles.

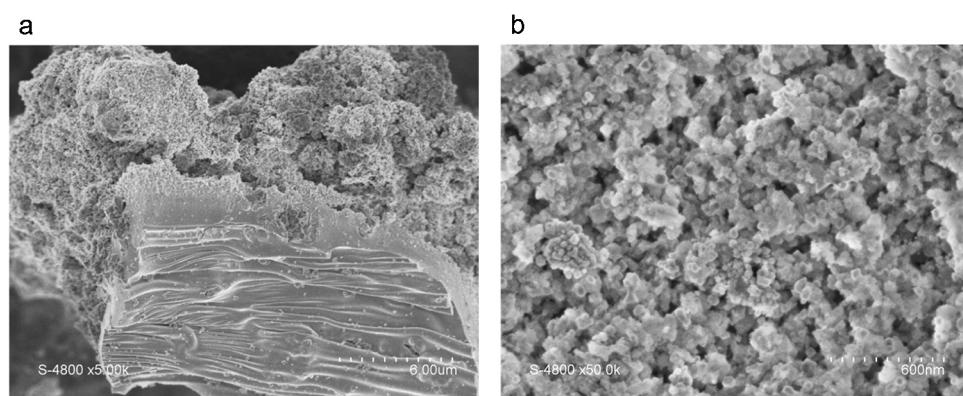


Fig. 5. SEM images of EcoNi(0).

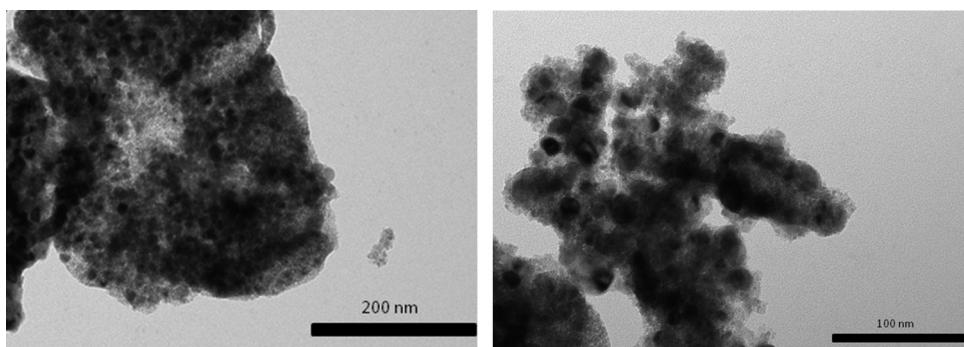


Fig. 6. TEM images of EcoNi(0).

Table 2
Optimization of the reaction conditions.

R ¹ O R ²		EcoNi(0) nanoparticles	i-PrOH, base, 80 °C	R ¹ OH R ²	
Entry	EcoNi(0) (mol%)	Base	Time (h)	Substrate	Yield (%) ^a
1	100	–	25	Cyclohexanone	29
2	10	NaOH 20 mol%	18	Cyclohexanone	56
3	10	NaOH 30 mol%	18	Cyclohexanone	100
4	1	NaOH 30 mol%	24	Cyclohexanone	100
5	1	Al ₂ O ₃ ^b	24	Cyclohexanone	100
6	–	Al ₂ O ₃ ^b	6	2-Dodecanone	11
7	1	Al ₂ O ₃ ^b	6	2-Dodecanone	93
8	–	Al ₂ O ₃ ^b	24	Acetophenone	9

Reaction conditions: ketone (1 mmol), i-PrOH (5 mL), EcoNi(0) (amount based on Ni), base, 80 °C.

^a Yield of the corresponding alcohol determined by GC-MS analysis.

^b Al₂O₃ basic Brockmann I activated, 1 g/1 mmol ketone.

3.2. Reduction of carbonyl compounds catalyzed by EcoNi(0)

3.2.1. Conditions of reduction

The catalytic properties of EcoNi(0) were assessed in the MPV reduction of carbonyl compounds. A preliminary study was conducted with cyclohexanone and 2-dodecanone, as model substrates (Table 2). Using EcoNi(0) alone, only a low yield of reduction product was observed for cyclohexanone (29%, entry 1), even with a stoichiometric amount of EcoNi(0), and after prolonged heating. However, addition of a catalytic amount of NaOH (20 mol%) allowed to lower the catalytic loading of EcoNi(0), while leading to a marked increase of reaction yield (56%, entry 2). The amount of EcoNi(0) could thus be reduced up to 1 mol%, by using 30 mol% NaOH, affording a quantitative reduction of cyclohexanone (entry 4). In spite of its efficiency, NaOH is a strong base, used in homogeneous phase in the reaction. We thus turned to alumina, a greener heterogeneous base. By using a ratio of one gram per mmol of ketone, alumina substituted for NaOH with the same efficiency, when associated to 1 mol% of EcoNi(0) (entry 5). Previous studies have reported the catalytic activity of alumina in MPV reduction of ketones, either at elevated temperatures (300 °C) [64], or with large amounts of solid (ca 5 g per mmol of substrate) [65], or in drastic conditions to avoid any trace of moisture [66]. In this context, we evaluated the activity of alumina in our experimental conditions, without EcoNi(0): whereas reduction of 2-dodecanone occurred with 93% yield by combining alumina and 1 mol% EcoNi(0), only 11% yield was observed with alumina alone, in the same conditions (entries 6–7). The example of acetophenone (entry 8) confirmed the very low reactivity of sole alumina in isopropanol. These results thus showed that alumina was almost not active in our conditions without EcoNi(0), and that ketone reduction occurred with high yield only when both species were associated. This observation is consistent with a number of previous reports, both in homogeneous

[26,67] and heterogeneous catalysis [27,28], where mechanistic studies have shown that addition of a base often promoted the interaction between isopropanol and the active metal species. It should be noted, that the amount of alumina could be reduced, but the reaction is slowed.

Although any attempt to directly reuse the EcoNi(0) failed, this methodology can be considered advantageous, because the addition of formic acid followed by the described thermic treatment (see part 3.1.1) allowed the regeneration and reuse of ecocatalyst. The properties of EcoNi(0) are preserved after regeneration.

3.2.2. Scope of the methodology

The conditions developed with EcoNi(0)/Al₂O₃ were applied to a range of carbonyl compounds, to assess the scope of the method (Table 3). The previous result of cyclohexanone reduction was further optimized with reduction of reaction time to 2 h (entry 1). These conditions were extended to the reduction of other ketones (entries 2–3 and 5–6), but long reaction time (24 h) remained necessary for complete reduction of acetophenone (entry 3). Aldehydes are challenging substrates for H-transfer reduction, especially in basic conditions, as they can easily undergo unwanted aldol condensation. For this reason, whereas H-transfer reduction of ketones has been described with a large number of catalysts, only a few have been reported for aldehydes [26]. In our case, reaction of 1-heptanal afforded 78% yield of 1-heptanol (entry 4), demonstrating that the catalytic system EcoNi(0)/Al₂O₃ was efficient for aldehyde reduction, with a minimal amount of side products. Interestingly, the conversion of benzaldehyde (entry 7, 99%) can be advantageously compared to literature (42 and 93%). [31–33,43] The catalytic system showed a high selectivity toward carbonyl compounds, as illustrated by the reduction of the aldehyde group of 3-nitrobenzaldehyde, without any reduction of the nitro group, even after a prolonged reaction time

Table 3
Scope of the EcoNi(0)-catalyzed H-transfer reduction.

Entry	Substrate	Time (h)	Product	Yield (%) ^a
1		2		>99
2		2		>99
3		24		>99
4		3		78 ^b
5		20		>99
6		6		93
7		2		99
8		18		83
9		18		85
10		24		75
11		4		>99
12		6		97 ^c

Reaction conditions: substrate (1 mmol), *i*-PrOH (5 mL), EcoNi(0) (1 mol%), Al₂O₃ basic Brockmann I activated (1 g), 80 °C.

^a Yield determined by GC-MS analysis.

^b Side products resulting of aldol condensation were formed in 18% yield.

^c Same *cis/trans* ratio for substrate and product: 24/76.

(entry 9). Similarly, the reduction of the aldehyde group of 4-cyanobenzaldehyde is chemoselective (entry 8). Contrary to Ni(0) nanoparticles described by Yus et al., our methodology is compatible with an alkyne moiety (entry 10) [68].

Finally, the catalytic system EcoNi(0)/Al₂O₃ revealed a high selectivity during the H-transfer reduction of α,β -unsaturated

aldehydes, like citral (entry 12). Reduction of citral can lead to a plethora of products, due to the combination of the three reducible groups. Whereas selective reduction of the carbonyl group is usually performed with catalysts based on precious metals like Pt, Au or Ir [69], EcoNi(0)/Al₂O₃ catalyzed citral reduction into geraniol in 97% yield. Moreover, no modification of the *cis/trans* ratio of

substrate occurred during reaction, conferring strong advantages to the EcoNi(0)/Al₂O₃ system as an alternative to expansive catalysts. Interestingly, the hydrogenation of citronellal with Ni/Al₂O₃ delivers citronellol, another compound used as fragrance ingredient (entry 11) [69]. We can conclude that Ni(0) and other elements present in EcoNi(0) demonstrate the interest of the original poly-metallic complexes of the plant-based catalyst.

4. Conclusion

In conclusion, we exploited the thermal reductive decomposition of biosourced Ni(II) formate made from the Ni hyperaccumulating plant *Psychotria gabriellae*, as an green alternative method for preparation of Ni(0), without hazardous and toxic reducing agents. Characterization of the resulting material EcoNi(0) confirmed that the material consists of agglomerated primary Ni(0) nanoparticles. Combined to alumina as a mild heterogeneous base, EcoNi(0) catalyzed the transfer hydrogenation of a range of carbonyl compounds, with isopropanol as an eco-friendly reagent and solvent. With only 1 mol% of EcoNi(0), ketones and aldehydes were reduced into alcohols, with high yield and selectivity. In particular, reduction of citral into geraniol, a molecule of commercial importance in the fragrance industry, highlighted the performances of the catalytic system as a valuable alternative to classical catalysts based on precious metals. The alternative we propose, using nickel hyperaccumulating plants to produce bio-based reducing agents could bring extra added value to the phytoextraction and the programs of ecological restoration.

Acknowledgements

This work was supported by the Agence Nationale de la Recherche (ANR, programme 11ECOT01101), the Agence de l'Environnement et de la Maîtrise de l'Energie (ADEME) and the Centre National de la Recherche Scientifique (CNRS). The authors are grateful to Société Le Nickel (SLN) and the South Province of New Caledonia for the facilities and financial support on mining sites.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2017.04.023>.

References

[1] I. Raskin, B.D. Ensley, *Phytoremediation of Toxic Metals: Using Plants to Clean up the Environment*, J. Wiley New York, 2000.

[2] C. Garbisu, I. Alkorta, Phytoextraction: a cost-effective plant-based technology for the removal of metals from the environment, *Bioresour. Technol.* 77 (2001) 229–236.

[3] J. Hunt Andrew, W.N. Anderson Christopher, N. Bruce, M. García Andrea, E. Graedel Thomas, M. Hodson, A. Meech John, T. Nassar Nedal, L. Parker Helen, L. Rylott Elizabeth, K. Sotiriou, Q. Zhang, H. Clark James, Phytoextraction as a tool for green chemistry, *Green Process. Synth.* 3 (2014) 3–22.

[4] A. Bhargava, F.F. Carmona, M. Bhargava, S. Srivastava, Approaches for enhanced phytoextraction of heavy metals, *J. Environ. Manage.* 105 (2012) 103–120.

[5] C. Grison, V. Escande, T.K. Olszewski, Ecocatalysis: a new approach toward bioeconomy, in: M.N.V. Prasad (Ed.), *Bioremediation and Bioeconomy*, Elsevier, Amsterdam, 2016, pp. 629–663.

[6] C. Grison, V. Escande, E. Petit, L. Garoux, C. Boulanger, C. Grison, *Psychotria douarrei* and *Geissois pruinosa*, novel resources for the plant-based catalytic chemistry, *RSC Adv.* 3 (2013) 22340–22345.

[7] C. Garel, B.-L. Renard, V. Escande, A. Galatyries, P. Hesemann, C. Grison, CC bond formation strategy through ecocatalysis: insights from structural studies and synthetic potential, *Appl. Catal. A* 504 (2015) 272–286.

[8] V. Escande, A. Velati, C. Garel, B.-L. Renard, E. Petit, C. Grison, Phytoextracted mining wastes for ecocatalysis: eco-Mn, an efficient and eco-friendly plant-based catalyst for reductive amination of ketones, *Green Chem.* 17 (2015) 2188–2199.

[9] V. Escande, B.-L. Renard, C. Grison, Lewis acid catalysis and Green oxidations: sequential tandem oxidation processes induced by Mn-hyperaccumulating plants, *Environ. Sci. Pollut. Res.* 22 (2015) 5633–5652.

[10] C.M. Grison, A. Velati, V. Escande, C. Grison, Metallophytes for organic synthesis: towards new bio-based selective protection/deprotection procedures, *Environ. Sci. Pollut. Res.* 22 (2015) 5686–5698.

[11] C.M. Grison, M. Mazel, A. Sellini, V. Escande, J. Biton, C. Grison, The leguminous species *Anthyllis vulneraria* as a Zn-hyperaccumulator and eco-Zn catalyst resources, *Environ. Sci. Pollut. Res.* 22 (2015) 5667–5676.

[12] ANR French National Research Agency, ANR's Annual Report 2014 <http://www.agence-nationale-recherche.fr/en/information/documents/annual-reports/> (Accessed January 2017).

[13] V. Escande, T.K. Olszewski, E. Petit, C. Grison, Biosourced polymetallic catalysts: an efficient means to synthesize underexploited platform molecules from carbohydrates, *ChemSusChem* 7 (2014) 1915–1923.

[14] V. Escande, E. Petit, L. Garoux, C. Boulanger, C. Grison, Switchable alkene epoxidation/oxidative cleavage with H₂O₂/NaHCO₃: efficient heterogeneous catalysis derived from biosourced eco-Mn, *ACS Sustain. Chem. Eng.* 3 (2015) 2704–2715.

[15] G. Clave, C. Garel, C. Poullain, B.-L. Renard, T.K. Olszewski, B. Lange, M. Shutcha, M.-P. Faucon, C. Grison, Ullmann reaction through ecocatalysis: insights from bioresource and synthetic potential, *RSC Adv.* 6 (2016) 59550–59564.

[16] C. Grison, V. Escande, Use of Certain Manganese-accumulating Plants for Carrying Out Organic Chemistry Reactions. PCT/FR2013/051772, 2013.

[17] C. Grison, V. Escande, Use of Certain Metal-Accumulating Plants for the Performance of Organic Chemistry Reactions. PCT/FR2013/050470, 2013.

[18] C. Grison, Use of Certain Organic Materials, Containing Alkali or Alkaline-earth Metals, for Implementing Organic Chemical Reactions. PCT/FR2014/052280, 2014.

[19] V. Escande, C.H. Lam, C. Grison, P.T. Anastas, EcoMnOx, a biosourced catalyst for selective aerobic oxidative cleavage of activated 1,2-Diols, *ACS Sustainable Chem. Eng.* 5 (4) (2017) 3214–3222.

[20] G. Losfeld, V. Escande, T. Jaffré, L. L'Huillier, C. Grison, The chemical exploitation of nickel phytoextraction: an environmental, ecologic and economic opportunity for New Caledonia, *Chemosphere* 89 (2012) 907–910.

[21] G. Losfeld, V. Escande, P. Vidal de La Blache, L. L'Huillier, C. Grison, Design and performance of supported Lewis acid catalysts derived from metal contaminated biomass for Friedel–Crafts alkylation and acylation, *Catal. Today* 189 (2012) 111–116.

[22] V. Escande, T.K. Olszewski, C. Grison, From biodiversity to catalytic diversity: how to control the reaction mechanism by the nature of metallophytes, *Environ. Sci. Pollut. Res.* 22 (2015) 5653–5666.

[23] Comprehensive organic synthesis II Reduction, Vol 8, second edition, Elsevier, Amsterdam, 2014.

[24] D. Sanfilippo, P.N. Rylander, Hydrogenation and Dehydrogenation, Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH & Co., 2016 (KGaA2000).

[25] A.J. Hunt, T.J. Farmer, J.H. Clark, Elemental Sustainability and the Importance of Scarce Element Recovery, Element Recovery and Sustainability, The Royal Society of Chemistry, Cambridge, 2013, pp. 1–28.

[26] X. Wu, J. Xiao, Reduction of CO to CHOH by metal-catalyzed hydrogenation and transfer hydrogenation, in: P. Knochel (Ed.), *Comprehensive Organic Synthesis II*, second edition, Elsevier, Amsterdam, 2014, pp. 198–273.

[27] G.K. Chuah, S. Jaenicke, Y.Z. Zhu, S.H. Liu, Meerwein-Ponndorf-Verley reduction over heterogeneous catalysts, *Curr. Org. Chem.* 10 (2006) 1639–1654.

[28] J.R. Ruiz, C. Jimenez-Sanchidrian, Heterogeneous catalysis in the Meerwein-Ponndorf-Verley reduction of carbonyl compounds, *Curr. Org. Chem.* 11 (2007) 1113–1125.

[29] F. Kazemi, A.R. Kiasat, Reduction of carbonyl compounds to the corresponding alcohols with isopropanol on dehydrated alumina under microwave irradiation, *Synth. Commun.* 32 (2002) 2255–2260.

[30] F. Alonso, Nickel Nanoparticles in the Transfer Hydrogenation of Functional Groups, *Metal Nanoparticles for Catalysis: Advances and Applications*, The Royal Society of Chemistry, Cambridge, 2014, pp. 83–98.

[31] F. Alonso, P. Riente, M. Yus, Nickel nanoparticles in hydrogen transfer reactions, *Acc. Chem. Res.* 44 (2011) 379–391.

[32] F. Alonso, P. Riente, M. Yus, Hydrogen-transfer reduction of carbonyl compounds catalysed by nickel nanoparticles, *Tetrahedron Lett.* 49 (2008) 1939–1942.

[33] F. Alonso, P. Riente, M. Yus, Hydrogen-transfer reduction of carbonyl compounds promoted by nickel nanoparticles, *Tetrahedron* 64 (2008) 1847–1852.

[34] F. Alonso, J.J. Calvino, I. Osante, M. Yus, Preparation of nickel(0) nanoparticles by arene-catalysed reduction of different nickel chloride-containing systems, *J. Exp. Nanosci.* 1 (2006) 419–433.

[35] F. Alonso, J.J. Calvino, I. Osante, M. Yus, A new straightforward and mild preparation of nickel(0) nanoparticles, *Chem. Lett.* 34 (2005) 1262–1263.

[36] A. Dhakshinamoorthy, K. Pitchumani, Clay entrapped nickel nanoparticles as efficient and recyclable catalysts for hydrogenation of olefins, *Tetrahedron Lett.* 49 (2008) 1818–1823.

[37] N. Neelakandeswari, G. Sangami, P. Emayavaramban, S. Ganesh Babu, R. Karvembu, N. Dharmaraj, Preparation and characterization of nickel

aluminosilicate nanocomposites for transfer hydrogenation of carbonyl compounds, *J. Mol. Catal. A: Chem.* 356 (2012) 90–99.

[38] D.-H. Chen, S.-H. Wu, Synthesis of nickel nanoparticles in water-in-Oil microemulsions, *Chem. Mater.* 12 (2000) 1354–1360.

[39] D.-H. Chen, C.-H. Hsieh, Synthesis of nickel nanoparticles in aqueous cationic surfactant solutions, *J. Mater. Chem.* 12 (2002) 2412–2415.

[40] S.-H. Wu, D.-H. Chen, Synthesis and characterization of nickel nanoparticles by hydrazine reduction in ethylene glycol, *J. Colloid Interface Sci.* 259 (2003) 282–286.

[41] V. Polshettiwar, B. Baruwati, R.S. Varma, Nanoparticle-supported and magnetically recoverable nickel catalyst: a robust and economic hydrogenation and transfer hydrogenation protocol, *Green Chem.* 11 (2009) 127–131.

[42] M. Kidwai, V. Bansal, A. Saxena, R. Shankar, S. Mozumdar, Ni-nanoparticles: an efficient green catalyst for chemoselective reduction of aldehydes, *Tetrahedron Lett.* 47 (2006) 4161–4165.

[43] M. Kidwai, N.K. Mishra, V. Bansal, A. Kumar, S. Mozumdar, Ni-nanoparticles usage for the reduction of ketones, *Catal. Commun.* 9 (2008) 612–617.

[44] D. Dutta, B.J. Borah, L. Saikia, M.G. Pathak, P. Sengupta, D.K. Dutta, Synthesis and catalytic activity of Ni^{2+} -acid activated montmorillonite nanoparticles, *Appl. Clay Sci.* 53 (2011) 650–656.

[45] Y. Wada, H. Kuramoto, T. Sakata, H. Mori, T. Sumida, T. Kitamura, S. Yanagida, Preparation of nano-sized nickel metal particles by microwave irradiation, *Chem. Lett.* (1999) 607–608.

[46] M. Tsuji, M. Hashimoto, T. Tsuji, Fast preparation of nano-sized nickel particles under microwave irradiation without using catalyst for nucleation, *Chem. Lett.* (2002) 1232–1233.

[47] J.C. Park, H.J. Lee, J.U. Bang, K.H. Park, H. Song, Chemical transformation and morphology change of nickel–silica hybrid nanostructures via nickel phyllosilicates, *Chem. Commun.* (2009) 7345–7347.

[48] G.P. Boldrini, D. Savoia, E. Tagliavini, C. Trombini, A. Umani-Ronchi, A new route to an active form of nickel. Transfer hydrogenation of alkenes and carbonyl compounds with 2-propanol, *J. Org. Chem.* 50 (1985) 3082–3086.

[49] M. Lerch, T. Ressler, F. Krumeich, J.-P. Cosson, E. Hnawia, A. Grohmann, Carbon-supported nickel nanoparticles from a wood sample of the tree *sebertia acuminata* pierre ex. Baillon, *Aust. J. Chem.* 63 (2010) 830–835.

[50] D.A. Dias, K.A. Kouremenos, D.J. Beale, D.L. Callahan, O.A.H. Jones, Metal and metalloid containing natural products and a brief overview of their applications in biology, biotechnology and biomedicine, *Biometals* 29 (2016) 1–13.

[51] S. Nishimura, Nickel from nickel formate, in: *Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis*, Wiley, New York, 2001, pp. 5–7.

[52] B. Xia, I.W. Lenggoro, K. Okuyama, Preparation of nickel powders by spray pyrolysis of nickel formate, *J. Am. Ceram. Soc.* 84 (2001) 1425–1432.

[53] W. Wang, M. Niu, Y. Hou, W. Wu, Z. Liu, Q. Liu, S. Ren, K.N. Marsh, Catalytic conversion of biomass-derived carbohydrates to formic acid using molecular oxygen, *Green Chem.* 16 (2014) 2614–2618.

[54] N. Müller, R. Romero, H. Grandón, C. Segura, Selective production of formic acid by wet oxidation of aqueous-phase bio-oil, *Energy Fuels* (2016).

[55] K.A. Hofmann, K. Schumpelt, Bildung von Formaldehyd und anderen organischen Stoffen aus Ameisensäure. I. Mitteilung;1; Selbstreduktion der Formiate, *Ber. Dtsch. Chem. Ges.* 49 (1916) 303–317.

[56] B.R. Wheeler, A.K. Galwey, Decomposition reactions of nickel formate, nickel malonate, nickel maleate and nickel fumarate in oxygen, *J. Chem. Soc. Faraday Trans. Phys. Chem. Condensed Phases* 70 (1974) 661–670.

[57] A.K. Galwey, M.E. Brown, The thermal decomposition of metal salts of organic acids – Nickel formate, in: *Thermal Decomposition of Ionic Solids*, Elsevier, Amsterdam, New York, 1999, pp. 442–443.

[58] I.E. Johnson, Manufacture of nickel formate. US Patent 2, 576 072, (1951).

[59] G. Losfeld, L. L'Huillier, B. Fogliani, S.M. Coy, C. Grison, T. Jaffré, Leaf-age and soil-plant relationships: key factors for reporting trace-elements hyperaccumulation by plants and design applications, *Environ. Sci. Pollut. Res.* 22 (2015) 5620–5632.

[60] G. Losfeld, R. Mathieu, L. L'Huillier, B. Fogliani, T. Jaffré, C. Grison, Phytoextraction from mine spoils: insights from New Caledonia, *Environ. Sci. Pollut. Res.* 22 (2015) 5608–5619.

[61] G. Losfeld, L. L'Huillier, B. Fogliani, T. Jaffré, C. Grison, Mining in New Caledonia: environmental stakes and restoration opportunities, *Environ. Sci. Pollut. Res.* 22 (2015) 5592–5607.

[62] R.E. Dinnebier, S.J.L. Billinge, *Powder Diffraction: Theory and Practice*, The Royal Society of Chemistry, Cambridge, 2008.

[63] K. Karakas, A. Celebioglu, M. Celebi, T. Uyar, M. Zahmakiran, Nickel nanoparticles decorated on electrospun polycaprolactone/chitosan nanofibers as flexible, highly active and reusable nanocatalyst in the reduction of nitrophenols under mild conditions, *Appl. Catal. B* 203 (2017) 549–562.

[64] D.V. Ramana, C.N. Pillai, Hydrogen transfer reactions. I. Reduction of carbonyl compounds by alcohols catalyzed by alumina, *Can. J. Chem.* 47 (1969) 3705–3707.

[65] G.H. Posner, A.W. Runquist, M.J. Chapdelaine, Organic reactions at alumina surfaces. 6. Isopropyl alcohol and diisopropylcarbinol on dehydrated alumina as reagents for very selective carbonyl reductions, *J. Org. Chem.* 42 (1977) 1202–1208.

[66] A.A. Wismeijer, A.P.G. Kieboom, H. van Bekkum, Conditioning of $\gamma\text{-Al}_2\text{O}_3$ catalyst in the transfer hydrogenation of 4-tert-butyl-cyclohexanone by 2-propanol, *Appl. Catal.* 34 (1987) 189–197.

[67] G. Zassinovich, G. Mestroni, S. Gladiali, Asymmetric hydrogen transfer reactions promoted by homogeneous transition metal catalysts, *Chem. Rev.* 92 (1992) 1051–1069.

[68] F. Alonso, I. Osante, M. Yus, Highly selective hydrogenation of multiple carbon–carbon bonds promoted by nickel(0) nanoparticles, *Tetrahedron* 63 (2007) 93–102.

[69] A. Stolle, T. Gallert, C. Schmoger, B. Ondruschka, Hydrogenation of citral: a wide-spread model reaction for selective reduction of alpha beta-unsaturated aldehydes, *RSC Adv.* 3 (2013) 2112–2153.